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Project Summary

Further Study of Adipic Acid Degradation in FGD Scrubbers

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The report gives results of investigations of adipic acid degradation to account for losses observed during earlier studies where it was used as an additive to improve SO_2 scrubber performance. Bench-scale experiments identified the major compounds resulting from the oxidative degradation of adipic acid, which are: valeric acid, glutaric acid, CO_2, CO, carbonate, methane, ethane, propane, and butane. Material balances based on various measurements—including gas chromatography, ion chromatography, and total organic carbon analyses—indicate that all by-products were identified in the laboratory tests: imbalances were less than 10% of the total carbon used. Field tests conducted on a prototype limestone scrubber using adipic acid additive detected only valeric acid and glutaric acid as degradation products. Scrubber sludge was shown to retain 200-500 ppm adipic acid by surface adsorption. In addition, the solids contained 300-800 ppm of occluded adipic acid when precipitated as calcium sulfite; occlusion was only 50 ppm when the solids were oxidized to gypsum.

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Introduction

This work under EPA Contract 68-02-2608, WA 72 is a continuation of EPA Contract 68-02-2607, WA 58 (EPA-600/7-79-224, September 1979). The objective of the first program was to determine the mechanism(s) of the degradation of adipic acid in a limestone, SO_2 wet scrubber. The adipic acid has been shown to promote SO_2 removal and limestone dissolution when added to the scrubbing solution at concentrations of a few thousand milligrams per liter. During tests with adipic acid, however, unaccounted losses of the acid have been observed.

Previous laboratory tests showed that the decomposition of adipic acid could occur through a chemical reaction. No indication of microbial degradation was observed. The chemical process responsible for at least part of the degradation is an oxidative, decarboxylation through a free radical reaction. The initial free radical is produced during the liquid phase oxidation of sulfite to sulfate. The products of this reaction identified to date are valeric acid, butyric acid, glutaric acid, succinic acid, methane, butane, and CO_2. However, the quantities of these products measured in laboratory tests and samples collected from EPA's RTP and Shawnee test facilities did not account for the difference between the quantity of adipic acid added to the systems and that leaving in the waste streams.

The objective of this phase of the study was to provide additional information into the fate of the adipic acid when used in the SO_2 scrubbers. The specific

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work areas conducted during this present program include:

1. more detailed investigation of the degradation products under laboratory simulated scrubber conditions;
2. development of improved analytical methods to quantify the organic content of the scrubber solids;
3. collection of samples around the oxidation vessels of the venturi/spray tower scrubber at the Shawnee facility for additional characterization of degradation products; and
4. identification of the compounds that contribute to the total organic content of the RTP and Shawnee scrubber liquor but were not previously measured by standard organic extraction techniques.

Summary of Results

Samples were collected and analyzed from EPA's prototype adipic acid scrubber at the Shawnee facility. Four organic material balances were calculated around the oxidizer tank in the venturi/spray tower scrubber at two different oxidation levels, 45% and 95%. Samples collected included inlet and outlet slurry streams and oxidizer vent gases. The following compounds were detected: adipic acid, valeric acid, glutaric acid, succinic acid, and carbon monoxide.

The rate at which adipic acid degraded in the oxidation tank was determined by the change in concentration between the oxidizer feed stream and the blowdown stream to thickener. This relation is stated mathematically in the following equation:

$$D.R. = [Ad]_i \cdot F_i - [Ad]_o \cdot F_o$$

where

D.R. = the degradation rate of adipic acid

$[Ad]_i$, $[Ad]_o$ = the adipic acid concentration in the oxidizer inlet and outlet streams, respectively, F_i, F_o = the flow rates of the oxidizer inlet and outlet streams, respectively.

During the low oxidation conditions, approximately 20% of the total adipic acid degradation in the system occurred within the oxidizer. Unexpectedly, the fraction of adipic acid loss across the oxidizer dropped to 10% when the oxidation was increased to 95%. However, the samples were collected when the scrubber system was in a mode of transition with respect to both pH and oxidation rate.

Total carbon material balances around the oxidizer closed to within ±10%. Valeric acid and glutaric acid were the main degradation products found. Succinic acid and carbon monoxide were minor contributors to the material balance. No light hydrocarbons were detected.

Samples of the scrubber solids were collected to determine whether adipic acid or any degradation products were being coprecipitated or adsorbed with these solids. In the previous adipic acid study, the techniques used to characterize the solids were not sensitive enough to detect concentrations below 1000 ppm. Even though concentrations of adipic acid in the solids much below 1000 ppm would not account for all of the losses, a method was developed to lower the detection limits to 10 ppm.

Most of the solid samples were washed after collection and the wash solutions were not retained. Therefore, except for one sample of the forced oxidized solids, only the coprecipitated fraction could be determined. However, solids collected from the laboratory studies were treated so that both retention mechanisms could be evaluated. The results of these measurements were:

1. scrubber solids consisting of more than 50% $CaSO_3 \cdot 1/2H_2O$ contained 300-800 ppm adipic acid in the coprecipitated form;
2. scrubber solids consisting of greater than 95% $CaSO_4 \cdot 2H_2O$ contained less than 50 ppm adipic acid in the coprecipitated form;
3. one filter cake sample consisting of greater than 95% $CaSO_4 \cdot 2H_2O$ was analyzed and found to have 215 ppm adipic acid adsorbed on the surface; and
4. fully oxidized solids from the laboratory studies were found to have 300-500 ppm adsorbed adipic acid and less than 50 ppm coprecipitated.

In the laboratory degradation studies conducted during this program, 60-99% of the adipic acid lost from solution was accounted for. Byproducts detected in the material balance tests included the following: valeric acid, glutaric acid, carbon dioxide, carbon monoxide, carbonate, methane, ethane, propane, and butane.

Conclusions

Based upon material balance tests conducted around the bleed stream oxidizer tank of the venturi/spray tower scrubber at the Shawnee facility, several observations were made.

1. The majority of the reported adipic acid loss did not take place in the oxidizer. Material balances performed under two different operating conditions indicate that only 10-20% of the total degradation occurred in the oxidizer.
2. Low molecular weight hydrocarbons were not detected in the Shawnee oxidizer vent.
3. Carbon monoxide, although identified, was not a significant degradation product in the Shawnee oxidizer.
4. Glutaric acid and valeric acid were the major degradation products identified.
5. Presumably, CO_2 is a degradation product under field conditions; however, the release of CO_2 during the dissolution of the limestone masks the contribution from degradation.

The analysis of the scrubber solids and the solids produced in the laboratory tests showed that as much as 1000 ppm adipic acid may be associated with the solids in low oxidation (<50%) cases. In the case of low oxidation, adipic acid losses have been reported at 20-50% amount added. The amount of adipic acid associated with solids can account for at least half of the losses. During forced oxidation conditions, the adipic acid losses are 50-90% higher. However, less adipic acid is associated solids and, thus, the amount removed with the solids accounts for only a small part of the observed losses. The remainder of the losses are, presumably, degradation.

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The complete report, entitled "Further Study of Adipic Acid Degradation in FGD Scrubbers," (Order No. PB 80 220155; Cost: $7.00, subject to change) will be available from:

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